VIBRATIONAL ENERGY DISPOSAL AND THE SPECTATOR MODEL FOR REACTION OF CH_3D WITH Cl

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Product state distributions for the reaction of vibrationally state selected CH_3D with Cl, $CH_3D(\nu)$ + Cl → CH_2D + HCl, reveal the extent to which vibrational energy initially deposited in the reactant survives in the CH_2D product. Infrared excitation prepares CH_3D in either the $\nu_1 + \nu_4$ (E) or the $2\nu_4$ (A_1, E) C-H stretching states and resonant enhanced multiphoton ionization (REMPI) detects the CH_2D. With $\nu_1 + \nu_4$ excitation, the reaction forms only vibrationally unexcited products, CH_2D (0_0), but $2\nu_4$ excitation forms CH_2D with stretch excited (1_1) and stretch-bend combination excited $(1_1 4_1)$ products. These results are consistent with the spectator model. In local mode notation, the $\nu_1 + \nu_4$ state corresponds to two quanta of excitation in the C-H bond ($|200\rangle|0\rangle$), and it reacts at the excited bond, giving all ground state CH_2D. The $2\nu_4$ state corresponds to excitation in two C-H bonds ($|110\rangle|0\rangle$), and in this case one excited C-H bond breaks while the other excited C-H bond remains in the products, resulting in an C-H stretch excited products.